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(54) **Title of the invention**

Method of production of an optical disk substrate.

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1. Title of the invention

Method of production of an optical disk substrate.

2. Scope of the patent

(1) Method for the production of an optical disk substrate by injection molding the resin resulting from the polymer portion having the aromatic vinyl monomer unit as the main ingredient and the polyphenylene ether portion where the temperature of the injected resin is kept between 300°C - 340°C.

3. Detailed description of the invention

(Fields of industrial usage)

This invention is concerned with the method of production of an optical disk substrate through the injection molding method and which has a remarkably small double refraction.

(Conventional techniques)

Using the laser optic spot, the record information that has been engraved on minute unevenness on the disk substrate is detected and the regeneration of the information record of high density is carried out by regenerating the image or sound or by changing the optical properties of the record engraved on the substrate surface. It is this regeneration of the record that has recently drawn attention.

The disk substrate that is used in such a system of record regeneration requires that it have transparency, the dimensional stability be good, it is optically homogenous, the double refraction be small and so on.

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With resin material being used as the disk substrate and even though large quantities of duplicated substrates can be molded at a low cost, in many cases molecular distribution occurs in the liquefaction as well as cooling process of the resin at the time of molding of the disk substrate. It is widely known that double refraction occurs which is said to be a fatal defect.

When it comes to actually using the resin material as a disk substrate, there is a demand that the double refraction be + 20 ~ -20 nm for a 546 nm as measured using the Senarmont Compensator method.

In US Patent Notification 4,373,065, it has been reported that the resin material has an exactly opposite optical anisotropy. Here, two types of polymer that melt completely are mixed in a composition that exactly nullifies that optical anisotropy and it results in an optically recorded element which is formed from an optically isotropic resin in which the double refractivity becomes practically zero.

In the said Patent Notification, it has also been mentioned that in the system of using polyphenylene ether and polystyrene as the polymers having an exactly opposite optical anisotropy, even if stress is applied on the film that is made from the composition of the mixture that exactly nullifies that optical anisotropy, double refraction does occur. In other words, when a polymer compound in a solid state is stretched, it was seen that double refraction did not occur.

(The problems that this invention seeks to solve)
The US Patent Notification 4,373,065 mentioned above does not mention as to how the double refractivity of the optical material becomes remarkably small when the optical material for the optical disk substrate is produced through injection molding using the polymer compound as the base material.

The optical anisotropy exists in the solid state. When two types of polymer that melt completely are mixed in a composition, the optical anisotropy in that solid state was seen to exactly contradict the mixture composition. When the substrate was molded

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through injection molding, it was found that the double refraction of the mold obtained was not necessarily small.

In other words, when an optical raw material for the optical card substrate is to be prepared through injection molding using the polymer compound as the raw material, the optical material having a small double refraction cannot be obtained merely by singularly matching the solid state optical anisotropy for individual polymers to the composition in which it has been thought of.

(Procedure for solving these problems)

In the method of production of an optical disk substrate through the injection molding method, the resin that is obtained from a polymer portion having an aromatic vinyl monomer unit as the main ingredient and the polyphenylene portion is subjected to injection molding and the special feature of this method is that the resin temperature is kept between 300C°C-340° C when molding is carried out.

The polymer having an aromatic vinyl monomer unit as the main ingredient, which is mentioned in this invention is the aromatic vinyl monomer-independent polymer and also it is the co-polymer, which has more than 50 weight % of an aromatic vinyl monomer unit. Styrene, α-methyl styrene, m-methyl styrene, ρ-methyl styrene, o-chlorostyrene, m-chlorostyrene, ρ-chlorostyrene, m-bromostyrene, ρ-bromostyrene etc. are examples of aromatic vinyl monomers, out of which styrene is the most desirable.

Examples of monomers that co-polymerize with aromatic vinyl monomers are unsaturated nitryl class compounds like acrylonitryl and methacrylonitryl; alkyl ester methacrylate class compounds like methyl methacrylate, n-propyl methacrylate, isopropyl methacrylate, n-butyl methacrylate, cyclohexyl methacrylate; alkyl acrylate class compounds like methyl acrylate, ethyl acrylate, propyl acrylate, butyl acrylate etc. There are also other compounds like methacrylic acid, acrylic acid, maleic anhydride, citraconic anhydride, N-methyl malemide, N-phenyl malemide etc. that can be used

The polymers that co-polymerize with these compounds can each be used either independently or as a mixture. It is better if the combination and regulation of the usage

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ratio of the co-polymer from the aromatic vinyl monomer as well as the resin material resulting from the aromatic vinyl monomer and polyphenylene ether are carried out without any hindrance.

It is desirable that the proportion of the aromatic vinyl monomer in the monomer mixture be more than 50 weight %. If the aromatic vinyl monomer is less than 50 weight % then the hygroscopic level of the resin becomes high, which is not desirable.

At a melt fluidity of 280°C and 8.8 kg. load, the polymer that has the aromatic vinyl monomer unit as the main ingredient has a melt flow rate of 0.5 ~ 200. However, the desirable range is 2 ~ 100.

If it exceeds 200, then the mechanical strength declines, which is not desirable and if it is less than 0.5 then reduction of double refraction becomes difficult, which is also not desirable.
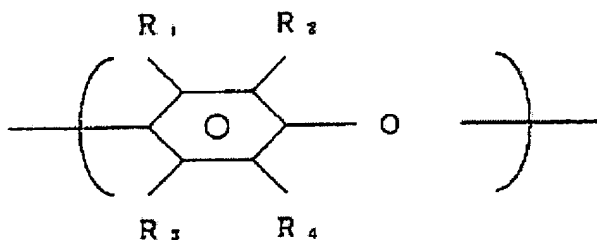
The method of production of the polymer that has the aromatic vinyl monomer unit as the main ingredient could be any of the methods that use a radical initiator such as block polymerization, suspension polymerization, emulsion polymerization or solvent polymerization. However keeping in mind the objective of obtaining a polymer with good productivity and having fewer impurities mixed in, block polymerization or suspension polymerization is desirable.

Peroxides like lauryl peroxide, benzoyl peroxide, di-tertiary butyl peroxide, di-cumyl peroxide and azo compounds like 2,2'-azobis-isobutylonitrile, 1,1'-azobis (1-cyclohexane carbonylnitrile) can be used a radical initiators.

To control the molecular weight, chain-transfer agents such as tert-butyl, n-butyl, n-octyl, n-dodecyl and tert-dodecyl mercaptane may be added.

Polymerization is generally carried out in the temperature range of 50 ~ 150°C.

The polyphenylene ether mentioned in this invention is represented in the general form and is a polymer that has repeating units.

$$-\left(\begin{array}{c} \overset{R_1}{\diagup} \quad \overset{R_2}{\diagdown} \\ O \\ \underset{R_3}{\diagdown} \quad \underset{R_4}{\diagup} \end{array} - O \right)-$$

(Here, R_1, R_2, R_3, R_4 indicates a hydrogen, halogen or a hydrogen carbide radical.)

The said polyphenylene ether is a polymer that has been polymerized from a phenol class monomer through oxide coupling. Polyphenylene ether is a compound that can be easily manufactured through known methods (Patent Notifications Sho 36-18692 and Sho 47-36518) using a copper group or manganese group catalyst.

Definite examples of polyphenylene ether are compounds such as poly(2, 6-dimethyl-1, 4-phenylene)ether, poly(2-methyl-6-ether-1, 4-phenylene)ether, poly(2-methyl-6-propyl-1, 4- phenylene)ether, poly(2, 6-dipropyl-1, 4-phenylene)ether, poly(2-methyl-6-bromo-1, phenylene)ether etc., out of which poly(2, 6-dimethyl-1, 4-phenylene)ether is preferred.

The average molecular weight of polyphenylene ether is obtained at the limiting viscosity of the polymer (measured in chloroform solution at 25°C) and is 0.1 ~ 1.01 however the desired weight is 0.3 ~ 0.7.

If the molecular weight is less than 0.1, then the double refraction of the optical resin material of this invention does not become sufficiently small and the strength also decreases.

If the molecular weight is more than 1.0, then the homogeneity of the optical resin material of this invention becomes low and further the melting fluidity becomes low.

To obtain the resin material by mixing a polymer that has the aromatic vinyl monomer as the main ingredient and polyphenylene ether, methods such as fusion mixing or solution mixing are suitable.

Fusion mixing is carried out in the presence of a solvent at a temperature higher than that of the glass transition temperature of the polyphenylene ether and under high shearing, for which mixing machines such as an extruder, Banbury mixer, kneader-blender, heat rolls etc. are used.

The degree of fusion should be to the extent that both the polymers are mutually dispersed and mixed upto approx 1 μ and further on they are mixed at the molecular level.

Whether the mixture state has reached the molecular level or not can be judged easily when the glass transition temperature of the mixture is a constant.

In order to obtain a very satisfactory mixture state, methods such as raising the mixing temperature, prolonging the mixing time and raising the shearing force are adopted.

Further in fusion mixing, to make the mixing easy by lowering the mixing temperature of both the polymers, small quantities of an organic solvent can be used as a plasticizer.

As for the organic solvent, the one that is used in the solvent mixing method mentioned in subsequent pages can be used here. After the mixing process is completed, it is better if the used organic solvent is removed through evaporation.

In solvent mixing, both the polymers are dissolved in the organic solvent and at least 1 weight % of the solvent is produced. After getting a uniform mixture through stirring, the organic solvent is removed through evaporation; alternatively, it is also

possible to add a low-solvent in both the polymers to obtain a uniform mixture and then precipitate the polymers that have been mixed.

The suitable organic solvents are chloroform, methylene chloride, ethylene chloride, toluene, benzene, chlorobenzene etc. Low-solvents are compounds such as methanol, ethanol, propyl alcohol, n-hexane, n-pentane etc.

The block co-polymer or graft co-polymer formed from the polymer portion having an aromatic vinyl monomer unit as the main ingredient and the polyphenylene ether portion is obtained by polymerizing the polymer on one side with the monomer on the other side.

In specific terms, as per the methods mentioned in Patent Notifications Sho 42-22069, Sho 47-1210, Sho 47-47862 and Sho 52-38596, the monomer that has the aromatic vinyl monomer as the main ingredient is polymerized in the presence of polyphenylene ether. Alternatively, the graft polymer or block co-polymer can be produced by polymerizing a phenol class monomer through oxide coupling in the presence of a polymer that has an aromatic vinyl monomer unit as the main ingredient.

The ratio of the polymer portion having the aromatic vinyl monomer unit as the main ingredient and the polyphenylene ether portion is 50 ~ 70 weight % of the former, preferably 55 ~ 65 weight %, to 30 ~ 50 weight % of the latter, preferably 35 ~ 45 weight %.

In the injection molding method mentioned in this invention, the process involves applying heat to the closed metal pattern cavity, injecting the resin in the fluid state into it, cold solidification and production of the mold item.

The process of applying heat within the metal pattern cavity could be by vacuum suction method or injection compression method where the metal cavity volume is reduced. Here, both the methods may be used together.

In the injection molding mentioned in this invention, the temperature of the resin that is injected is between 300-340°C; however a temperature of 305°C to 335°C would be desirable.

The resin temperature mentioned here is the temperature of the resin that has undergone plasticized fusion in the injection cylinder of the injection-molding machine.

If the resin temperature is below 300°C, then the measurement of double refraction of the optical disk substrate carried out through the Senarmont Compensator at 546 nm will be more than 20 nm and would therefore be unsuitable as an optical disk substrate. And again, if the resin temperature exceeds 340°C, then poor results such as dissolution of the resin, yellowing, silvering etc occur and the pit error of the optical disk substrate increases remarkably.

In the injection molding method of this invention, it is desirable that the temperature of the metal pattern cavity is maintained above 80°C and below 120°C; however a more desirable range would be between 85°C to 115°C.

The metal pattern temperature mentioned here is the surface temperature of the metal cavity immediately before the injection.

If the metal temperature is below 80°C, then the transference of the minute guide grooves (group) that have been engraved on the surface of the metal pattern becomes bad. And again, if the metal temperature exceeds 120°C, then the mold release from the metal becomes bad, which is not desirable.

In the injection molding method of this invention, it is desirable that molding is carried out in a dwell time ranging from 0.2 seconds to 3 seconds. However, a more desirable range would be above 0.3 seconds and below 0.2 seconds.

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The dwell time mentioned here is the time taken for replenishing the resin in the metal cavity.

If the dwell time is below 0.2 seconds, then a silver streak is generated and when it is used as an optical disk, the pit error increases remarkably. If the time exceeds 3 seconds, then the double refraction of the optical disk (obtained through the Senarmont Compensator method at 546 nm) goes above 20 nm, which is not desirable.

In the said dwell time, the resin quantity corresponding to this time is approx. 5g/sec ~ approx. 75 g/sec.

As explained above, whether it is formed from the resin portion having an exactly opposite optical anisotropy or it is a resin of the composition that just nullifies the optical anisotropy, the optical anisotropy is manifested in the injection molding method and when it is used as an optical disk, an undesirable double refraction occurs.

It is thought that this is because during injection molding, each of the resin components having an exactly opposite optical anisotropy has a different orientation conduct or it has a different moderation time.

In other words, even if it is a resin of the composition that nullifies the said optical anisotropy, if it is not according to the injection molding prescribed in this invention, then it is not possible to make an optical disk substrate with a small optical anisotropy.

(Application examples)

The injection-molding machine used in the Application Examples was a Sumitomo Heavy Machinery Industries-make Neomatt Model 150/75; the metal pattern had a mold diameter of 120 mm and a metal pattern for compact disks (with a built-in Stamper) having a thickness of 1.2 mm was used.

The double refraction of the disk substrate was measured through the Senarmont Compensator method using a polarized microscope and laser rays of wavelength 546 nm.

The measurement positions in the disk substrate were at a distance of 25 mm, 40 mm and 55 mm from the center to the radius.

The mold transference was evaluated in such a way that when the depth in the mold group was more than 80% as against the depth in the stamper groove; it was passed (marked as O).

Regarding the release of the mold product, the existence of a mold-release line was confirmed through visual observation using a polarized light plate.

Application Examples 1 ~ 2, Comparative Examples 1 ~ 2

41.5-weight portion of poly(2, 6 – dimethyl–1,4–phenylene)ethyl having a limiting viscosity of 0.52 measured in a chloroform solvent at 25°C and 58.5-weight portion of polystyrene (Japan Polystyrene Corporation Esbrite® 8 - 62A) were mixed and pelletized in a bi-axial extruder (Japan Steel Works-make, Model TEX 30-30BW-2V).

This pellet was molded through an injection-molding machine with the resin temperature as shown in Table 1, the metal pattern temperature at 100°C and an injection molding time of 1 second.

The double refraction and appearance of the optical disk substrate is shown in Table 1.

Table 1

	Resin temperature °C	Double Refraction (nm)			Appearance
		25 mm	40 mm	55 mm	
Comparative Example 1	290	- 25	- 13	- 9	Good
Application Example 1	310	-8	- 7	- 5	Good
Application Example 2	330	-2	0	- 2	Good
Comparative Example 2	350	2	0	- 8	Yellowing occurred

Application Examples 3 ~ 6, Comparative Examples 3 ~ 4

Using the pellet given in Application Example 1, molding was carried out through the injection-molding machine at a resin temperature of 320°C, injection time of 1 second and metal pattern temperature as shown in Table 2.

The transference and mold release of the optical disk substrate obtained is shown in Table 2.

Table 2

	Metal Pattern temperature °C	Transference	Mold release
Comparative Example 3	75	X	No
Application Example 3	90	O	No
Application Example 4	95	O	No
Application			

Example 5	115	O	No
Application Example 6	120	O	Scantily present
Comparative Example 4	125	O	Yes

Application Examples 7 ~ 11, Comparative Examples 5 ~ 6

Using the pellet given in Application Example 1, injection molding was carried out through the injection-molding machine at a resin temperature of 320°C, metal pattern temperature of 100° and injection time as shown in Table 2.

The double refraction and appearance of the optical disk substrate obtained is shown in Table 3.

<u>Table 3</u>

	Injection time (Seconds)	Double Refraction (nm)			Appearance
		25 mm	40 mm	55 mm	
Comparative Example 5	0.1	- 23	- 16	- 12	Silver streak
Application Example 7	0.3	-16	- 10	- 6	O
Application Example 8	1.0	-5	- 3	- 4	O
Application Example 9	1.8	10	7	4	O
Application Example 10	2.5	14	12	9	O
Application					

Example 11	3.0	18	16	11	O
Comparative Example 6	3.5	26	24	20	O

Effect of this invention

As explained above in detail, even if an optical disk substrate is prepared singly through the injection molding method using the resin formed from the polymer portion having an aromatic vinyl monomer unit as the main ingredient and polyphenylene portion composition that nullifies each of the exactly opposite optical anisotropy in the solid state, it is not possible to easily produce an optical disk substrate that has a remarkably small double refraction.

By carrying out molding according to the injection molding method of this invention, for the first time it has become possible to obtain an optical disk substrate having a remarkably small double refraction.

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